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(54) Title: CATIONIC DYES FOR KERATIN-CONTAINING FIBRES

(57) Abstract

Keratin-containing fibres, in particular human hair, are dyed using dyes using dyes of formulae (1) to (9) indicated in claim 1.

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Cationic dyes for keratin-containing fibres

The present invention relates to a process for dyeing keratin-containing fibres, in particular human hair, with cationic dyes.

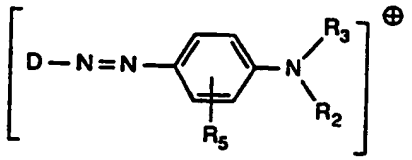
By far the largest proportion of all hair dyeings are carried out, even today, using so-called "oxidation colours", which involves applying small, colourless precursor molecules to the hair and reacting them by an oxidation process to form larger, coloured molecules. Although this produces the most durable ("permanent") colourings, increasing reservations are being voiced about possible toxicological risks posed not only by the substances used as starting materials but also by the oxidation intermediate and end products, whose precise composition is virtually uncontrollable. Further disadvantages are the relatively complicated use and in particular also the hair damage due to the aggressive chemicals used.

The other, so-called "semipermanent" and "temporary" colourings involve the use of ready-prepared dyes, specifically primarily uncharged disperse dyes and relatively sparingly water-soluble acid dyes. Cationic dyes, by contrast, play only a very minor part. As the terms "semipermanent" and "temporary" indicate, these colourings only have a medium to poor fastness level. Especially the cationic dyes have a reputation for poor hydrolysis and light resistance and for uneven colouring of the hair, for example between root and tip (see: John F. Corbett: The Chemistry of Hair-care Products, JSDC August 1976, p. 290). In addition, the known cationic dyes have an insufficient build-up; i.e., even if increased amounts are used, it is impossible to exceed a certain, relatively low, colour strength. For instance, it is not possible to achieve a deep black coloration with the most important cationic hair dyes Basic Yellow 57, Basic Red 76, Basic Blue 99, Basic Brown 16 and Basic Brown 17 which are used in practice. For the same reason it is difficult to tint relatively dark natural hair with these dyes.

It has now been found that surprisingly cationic dyes of the below-indicated formulae have none of these disadvantages. They can be used to achieve in a very simple way and under gentle conditions very deep dyeings having excellent light, shampooing and crock fastness properties. Owing to their extremely clean shades, they also extend the range of possible mixed shades considerably, especially in the direction of the increasingly important brilliant fashion colours.

fastness properties. Owing to their extremely clean shades, they also extend the range of possible mixed shades considerably, especially in the direction of the increasingly important brilliant fashion colours.

The present invention accordingly provides a process for dyeing keratin-containing fibres, which comprises treating the fibres with a dye of the formula



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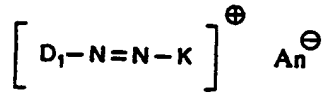

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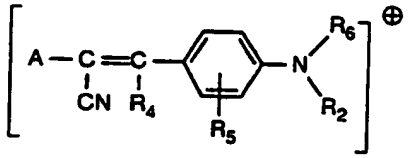

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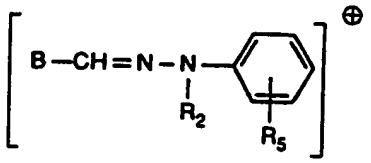

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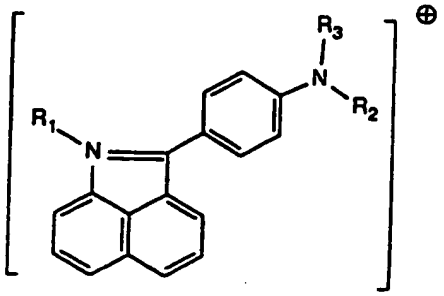

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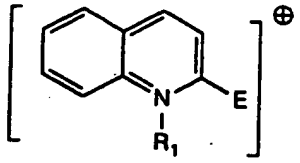

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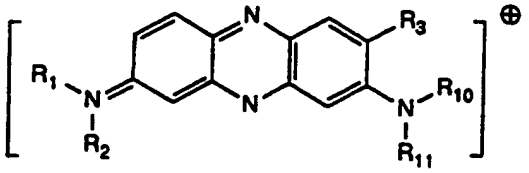

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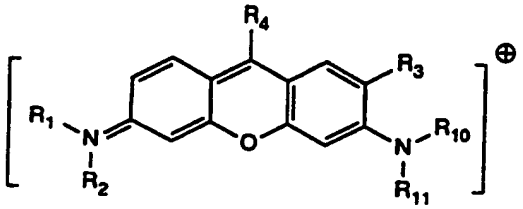
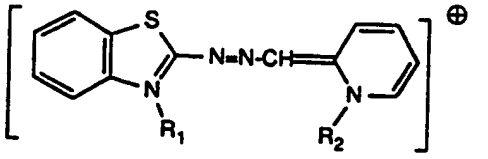


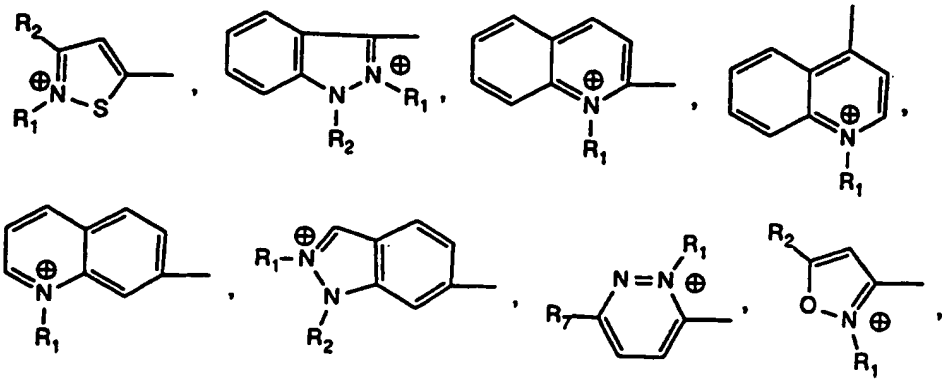
(8) or

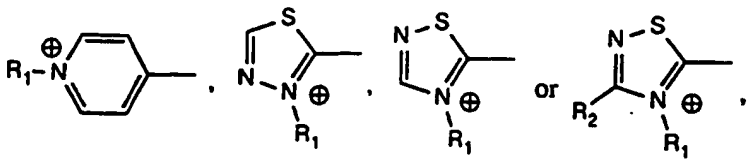


(9)

where

D is the radical of a diazo component of the formula





R_1 is unsubstituted or OH-, C_1-C_4alkoxy-, halogen-, CN-, amino-, C_1-C_4monoalkylamino- or di-C_1-C_4alkylamino-substituted C_1-C_4alkyl,

R_2 and R_3 are independently of each other hydrogen or unsubstituted or OH-, C_1-C_4alkoxy-, halogen-, CN-, amino-, C_1-C_4monoalkylamino- or di-C_1-C_4alkylamino-substituted C_1-C_4alkyl, or

R_3 and R_2 are together with the nitrogen atom joining them together a 5- or 6-membered ring,

R_4 is hydrogen or CN,

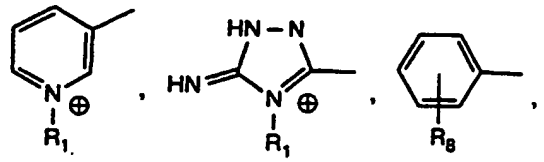
R_5 is hydrogen, C_1-C_4alkoxy, halogen, C_1-C_4alkyl or C_1-C_4alkylcarbonylamino, or

R_5 and R_2 are together with the nitrogen and carbon atoms joining them together a 5- or 6-membered ring,

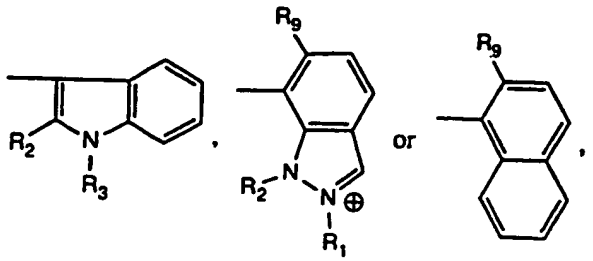
R_6 is hydrogen or unsubstituted or OH-, C_1-C_4alkoxy-, halogen-, CN-, amino-, C_1-C_4monoalkylamino-, di-C_1-C_4alkylamino- or tri-C_1-C_4alkylammonium-substituted C_1-C_4alkyl,

R_7 is hydrogen, unsubstituted or OH-, C_1-C_4alkoxy-, halogen-, CN-, amino-, C_1-C_4monoalkylamino- or di-C_1-C_4alkylamino-substituted C_1-C_4alkyl or C_1-C_4alkoxy,

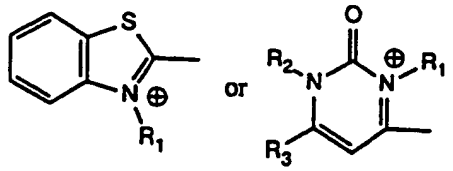
D_1 is the radical of a diazo component of the formula



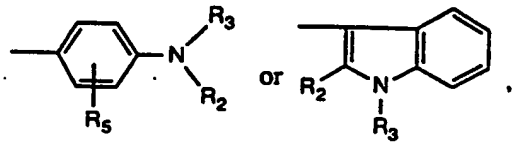
K is the radical of a coupling component of the formula



with the proviso that either D_1 or K carries a cationic charge,
R_8 is hydrogen, C_1-C_4alkyl, C_1-C_4alkoxy, halogen or amino,
R_9 is hydroxyl or amino
A is CN or tri-C_1-C_4alkylammonium-substituted C_1-C_4alkoxycarbonyl,
B is a radical of the formula



E is a radical of the formula



R_{10} and R_{11} are independently of each other hydrogen or unsubstituted or OH-, C_1-C_4alkoxy-, halogen-, CN-, amino-, C_1-C_4monoalkylamino- or di-C_1-C_4alkylamino-substituted C_1-C_4alkyl, or
R_{10} and R_{11} are together with the nitrogen atom joining them together a 5- or 6-membered ring, and
$An^{\ominus}$ is a colourless anion.

For the purposes of the present invention, alkyl radicals are generally straight-chain or branched C_1-C_4alkyl groups. Suitable are for example methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl or tert-butyl.

Suitable alkoxy radicals are those having 1 to 4 carbon atoms, e.g. methoxy, ethoxy, propoxy, isopropoxy, n-butoxy, isobutoxy or tert-butoxy.

Halogen is to be understood as meaning fluorine, bromine, iodine or in particular chlorine.

If R_5 and R_2 are combined with the nitrogen atom and the two carbon atoms joining them together into a 5- or 6-membered ring, this ring may contain a further heteroatom, for example oxygen or sulfur. Moreover, the ring may be substituted, for example by

hydroxyl, alkoxy, alkyl, halogen, CN or phenyl, or carry a further fused-on benzene ring. Preferred rings formed by R_5, R_2, the linking carbon atoms and the nitrogen atom are pyrroline, dihydrooxazine and di- or tetrahydropyridine rings carrying 0 to 4 methyl groups.

R_2 and R_3 can also combine with the nitrogen atom joining them together to form a piperidine, morpholine or piperazine radical. The piperazine radical can be substituted at the nitrogen atom which is not bonded to the phenyl ring by C_1-C_4alkyl or hydroxy-C_1-C_4alkyl or amino-C_1-C_4alkyl. The preferred substituent is hydroxyethyl.

Suitable anions $An^{\ominus}$ include organic as well as inorganic anions, for example chloride, bromide, sulfate, hydrogensulfate, methosulfate, phosphate, borotetrafluoride, carbonate, bicarbonate, oxalate, formate, acetate, propionate, lactate or complex anions, such as the anion of zinc chloride double salts.

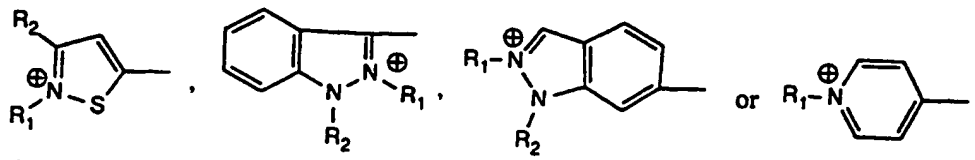
The anion is generally given by the method of preparation. Preferred anions are chloride, sulfate, hydrogensulfate, methosulfate, phosphate, formate, acetate or lactate.

To dye by the process of the invention it is preferable to use a dye of the formula (1) or (2).

Of the dyes of the formula (1), particular preference is given to those where R_1 is unsubstituted C_1-C_4alkyl, especially methyl or ethyl.

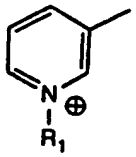
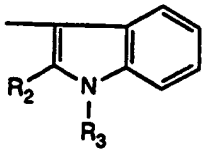
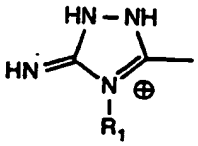
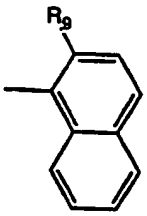
Particular preference is also given to dyes of the formula (1) where R_2 and R_3 are independently of each other hydrogen or unsubstituted C_1-C_4alkyl, especially methyl or ethyl, and to those where R_5 is hydrogen, methoxy, ethoxy, chlorine, methyl or ethyl.

Of the dyes of the formula (1), particular preference is further given to those where D is the radical of a diazo component of the formula



where R_1 is unsubstituted C_1-C_4alkyl, especially methyl or ethyl, and R_2 is hydrogen or

unsubstituted C_1-C_4alkyl, especially methyl or ethyl.

Preferred dyes of the formula (2) are those where D_1 is the radical of a diazo component of the formula  and K is the radical of a coupling component of the formula  and those where D_1 is the radical of a diazo component of the formula  and K is the radical of a coupling component of the formula  where R_1 is unsubstituted C_1-C_4alkyl, especially methyl or ethyl, R_2 and R_3 are independently of each other hydrogen or unsubstituted C_1-C_4alkyl, especially methyl or ethyl, and R_9 is hydroxyl or amino.

In the dyes of the formula (3), either the radical A or the radical R_6 has to carry a trialkylammonium group.

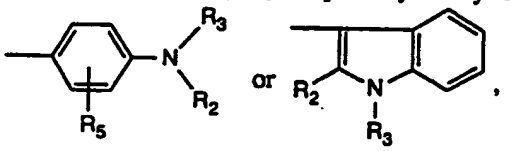
Preferred dyes of the formula (3) are those where A is CN, R_5 is hydrogen or unsubstituted C_1-C_4alkyl, especially methyl or ethyl, R_2 is unsubstituted C_1-C_4alkyl, especially methyl or ethyl, and R_6 is tri-C_1-C_2alkylammonium.

A trialkylammonium group A in the dyes of formula (3) is preferably a tri-C_1-C_2alkylammonium group. In such dyes, R_2 and R_6 are preferably independently of each other hydrogen or unsubstituted C_1-C_4alkyl, especially methyl or ethyl, and R_5 is preferably hydrogen, methoxy, ethoxy, chlorine, methyl or ethyl.

In preferred dyes of formula (4), R_1 is unsubstituted C_1-C_4alkyl, especially methyl or ethyl, and R_2 and R_5 are independently of each other hydrogen or unsubstituted C_1-C_4alkyl, especially methyl or ethyl.

Of the dyes of the formula (5), particular preference is given to those where R_1 is unsubstituted C_1-C_4alkyl, especially methyl or ethyl.

Particular preference is also given to the dyes of the formula (5) where R_2 and R_3 are independently of each other hydrogen or unsubstituted C_1-C_4alkyl, especially methyl or ethyl.

In a dye of formula (6), preferably R_1 is unsubstituted C_1-C_4alkyl, especially methyl or ethyl, and E is a radical of the formula  where R_2 and R_3 are independently of each other hydrogen or unsubstituted C_1-C_4alkyl, especially methyl or ethyl, and R_5 is hydrogen or unsubstituted C_1-C_4alkyl, especially hydrogen.

Of the dyes of the formula (7), preference is given to the use of those where R_1 is unsubstituted C_1-C_4alkyl, especially methyl or ethyl.

Particular preference is also given to dyes of the formula (7) where R_2 and R_3 are independently of each other hydrogen or unsubstituted C_1-C_4alkyl, especially methyl or ethyl, and R_{10} and R_{11} are each hydrogen.

In a dye of the formula (8), preferably R_1 is unsubstituted C_1-C_4alkyl, especially methyl or ethyl.

Particular preference is also given to dyes of the formula (8) where R_2, R_3, R_{10} and R_{11} are each independently of the others hydrogen or unsubstituted C_1-C_4alkyl, especially methyl or ethyl.

Of the dyes of the formula (9), preference is given to using those where R_1 and R_2 are each unsubstituted C_1-C_4alkyl, especially methyl or ethyl.

The dyes of the formulae (1) to (9) are known or can be prepared in a manner known per se.

The present invention further provides a process for dyeing keratin-containing fibres, which comprises treating the fibres with a mixture of at least two cationic dyes of the formulae (1) to (9).

Preference is given to using a mixture of at least three cationic dyes of the formulae (1) to (9) and in particular to a mixture of a yellow, a red and a blue cationic dye of the formulae (1) to (9).

The processes of the invention are suitable for dyeing furs and also animal and human hair, especially live human hair and domestic animals' hair. As a consequence of the high affinity and the good water solubility of the dyes used, it is possible to do the dyeing at room temperature from aqueous solutions without any assistants whatsoever.

However, it is also possible to use any customary cationic dye assistants used in the dyeing of hair, for example wetting agents, swelling agents, penetration aids or scents. In addition, the dyes can be incorporated into shampoos, creams, gels or pastes. Such cosmetic formulations for dyeing hair comprising at least one dye of the above-indicated formulae (1) to (6) and also assistants form a further part of the subject-matter of the present invention.

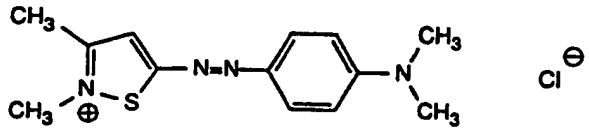
A particular advantage of the dyes used according to the invention for dyeing hair is that, owing to the good build-up of the dyes, the colourings can be prepared by the trichromatic principle; that is, it is possible by using a yellow, a red and a blue dye in suitable mixtures of these dyes to achieve virtually all shades. In addition, exact prediction of the shades obtained is possible, which is not the case with the so-called "oxidation dyes" owing to the varying composition of the end products.

Using colorimetric methods of measurement it is also possible to obtain on natural, unbleached hair predicted shades having regard to the hair's natural colour by determining its yellow, red and blue content and deducting it from the recipe of the desired shade. This is not feasible with the hair dyes previously used.

The colourings obtained are crock-, water-, wash- and light-fast and stable to permanent-deformation agents, for example thioglycolic acid.

The Examples which follow illustrate the invention. Parts and percentages are by weight. The temperatures are given in degrees Celsius.

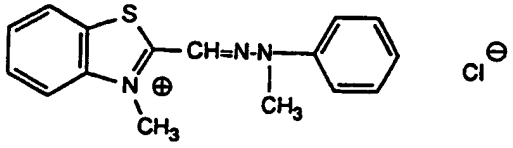
Example 1: A braid-sewn strand of blond, natural, untreated human hair is dyed at 25°C for 5 minutes in a conventional manner with a dye emulsion containing 0.1 % of the blue dye of the formula



3.5 % of Cetearyl Alcohol
1.0 % of Ceteareth 80
0.5 % of glyceryl mono-di-stearate
3.0 % of stearamide DEA
1.0 % of stearamphopropylsulfonate
0.5 % of polyquaternium-6 and
water to 100 %.

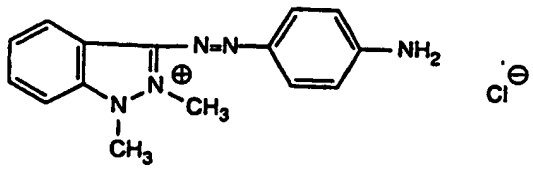
Then the hair is thoroughly rinsed with water and air-dried. The result is an intensive brilliant blue colouring. The light, shampooing and friction fastness properties of the colouring according to the invention are excellent.

Example 2: Example 1 is repeated with the dye of the formula



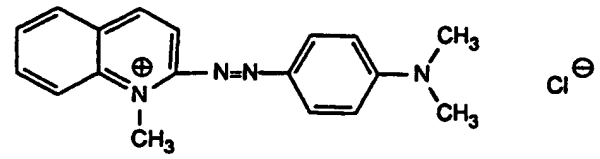
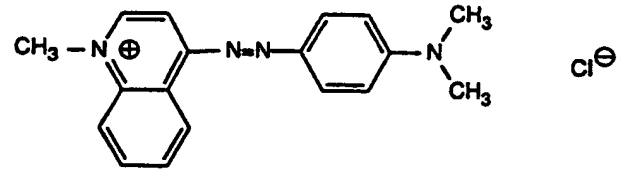
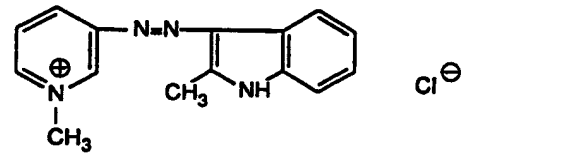
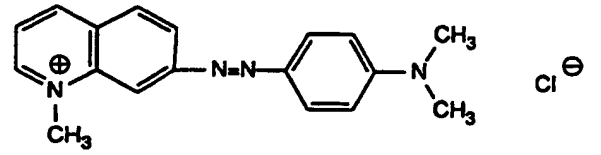
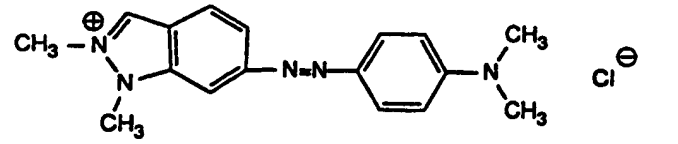
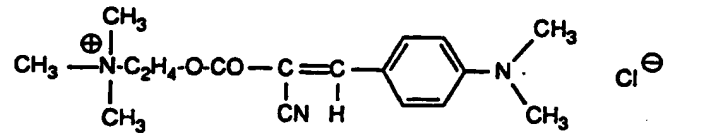
affording an intensively yellow colouring with likewise excellent fastness properties.

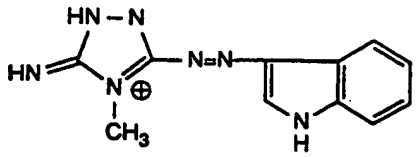
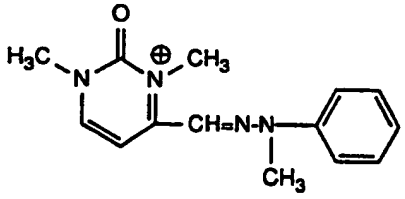
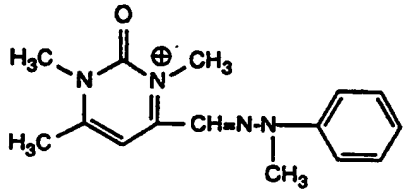
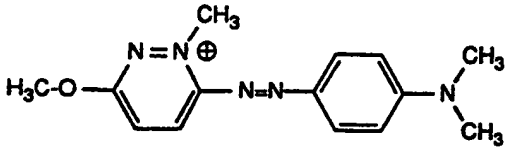
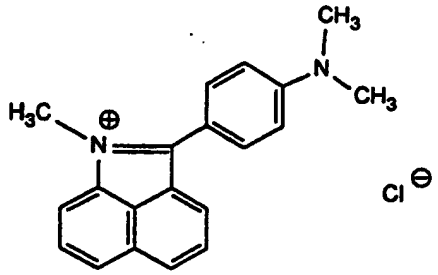
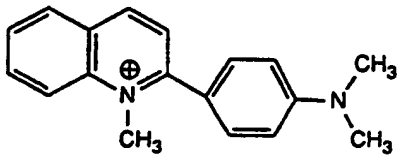
Example 3: A 1 % solution of the dye of the formula

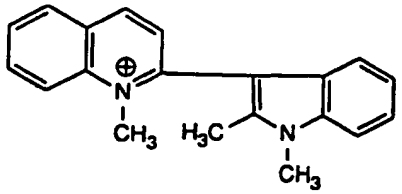


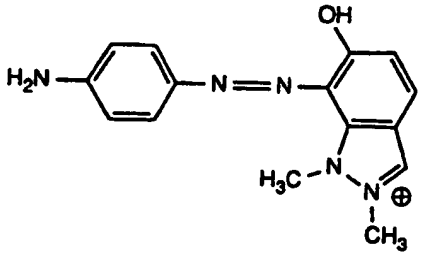
in a surfactant base containing 10 % of cocoamphoglycinate and 90 % of water is applied to Chinese, bleached yak hair at 25°C for 5 minutes, and then the hair is thoroughly rinsed and air-dried. An intensively red colouring is obtained with good light fastness.

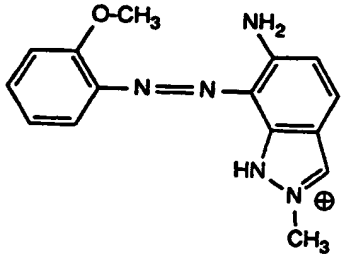
Examples 4-35: The method of Examples 1-3 is applied with the dyes listed below in the table, affording colourings on the hair in the specified hues.

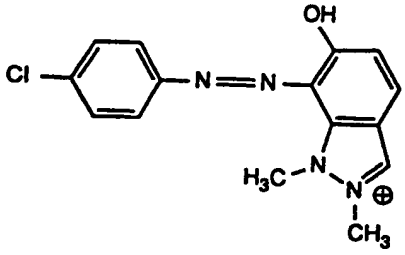
Example	Dye	Hue
4		blue
5		blue
6		yellow
7		orange
8		reddish orange
9		yellow

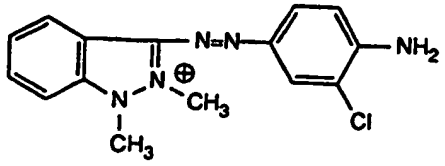
10		$Cl^{\ominus}$	reddish yellow
11		$Cl^{\ominus}$	yellow
12		$Cl^{\ominus}$	yellow
13		$Cl^{\ominus}$	reddish bluish violet
14		$Cl^{\ominus}$	bluish violet
15		$Cl^{\ominus}$	orange

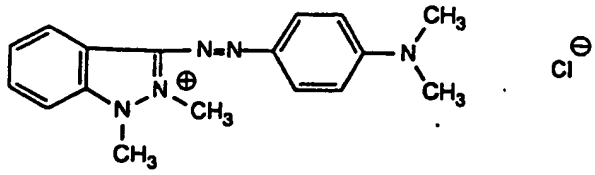
16  $Cl^{\ominus}$ yellow

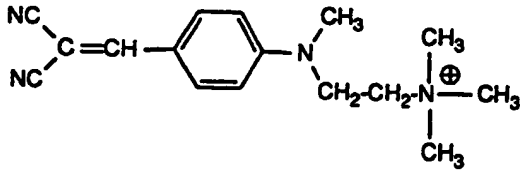
17  $Cl^{\ominus}$ brown

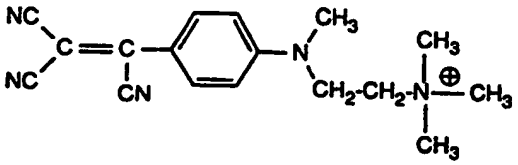
18  $Cl^{\ominus}$ red

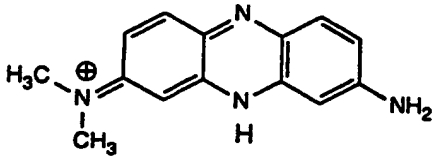
19  $Cl^{\ominus}$ yellow

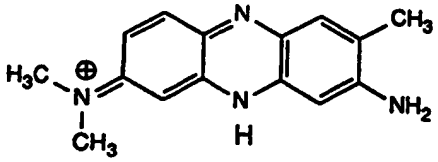
20  $Cl^{\ominus}$ scarlet

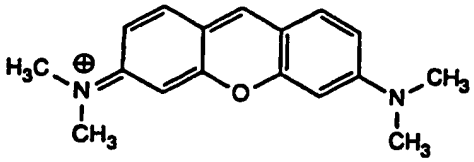
21  violet

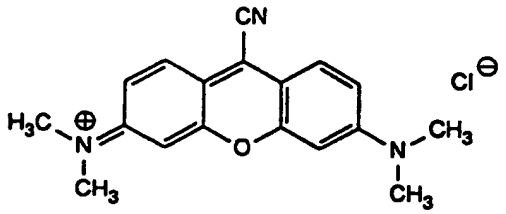
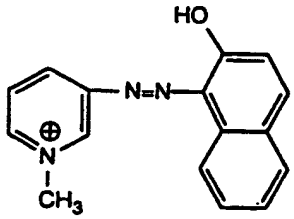
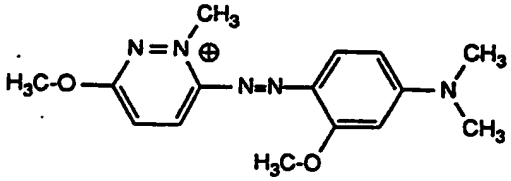
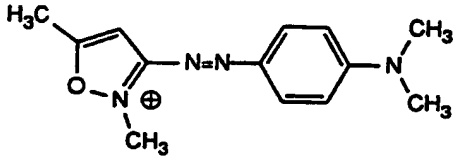
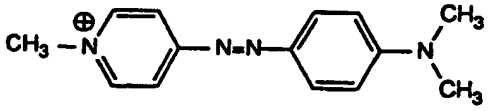
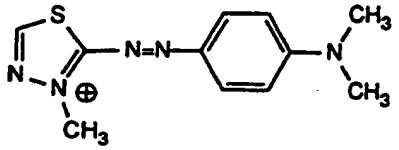
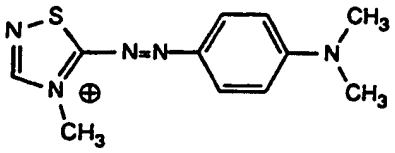
22  yellow

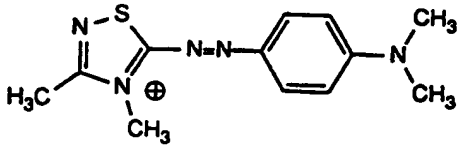
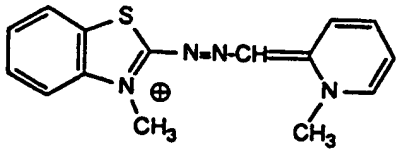
23  red

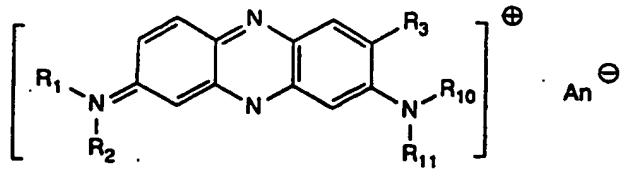
24  violet (neutral)

25  red (neutral)

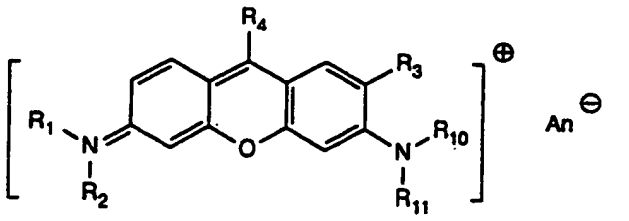
26  red

27			blue
28		$Cl^{\ominus}$	yellow
29		$Cl^{\ominus}$	red
30		$Cl^{\ominus}$	red
31		$Cl^{\ominus}$	violet
32		$Cl^{\ominus}$	violet
33		$Cl^{\ominus}$	violet

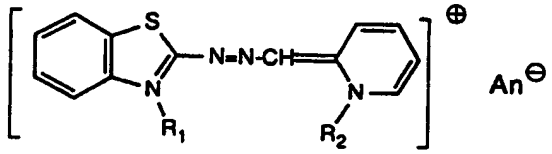
34		$Cl^{\ominus}$	violet
35		$Cl^{\ominus}$	yellow



(7),



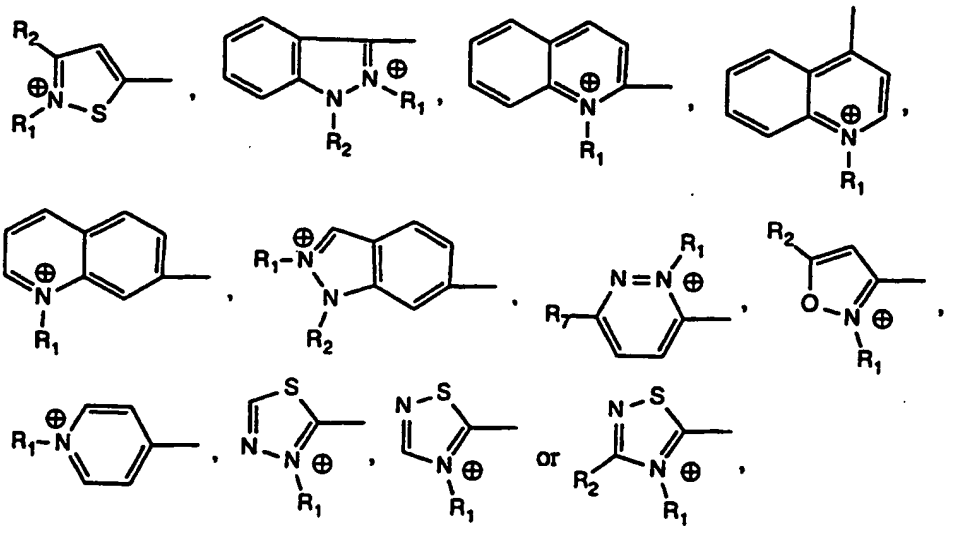
(8) or



(9)

where

D is the radical of a diazo component of the formula



R_1 is unsubstituted or OH-, C_1-C_4alkoxy-, halogen-, CN-, amino-, C_1-C_4monoalkylamino- or di-C_1-C_4alkylamino-substituted C_1-C_4alkyl,

R_2 and R_3 are independently of each other hydrogen or unsubstituted or OH-, C_1-C_4alkoxy-, halogen-, CN-, amino-, C_1-C_4monoalkylamino- or di-C_1-C_4alkylamino-substituted C_1-C_4alkyl, or

R_3 and R_2 are together with the nitrogen atom joining them together a 5- or 6-membered ring,

R_4 is hydrogen or CN,

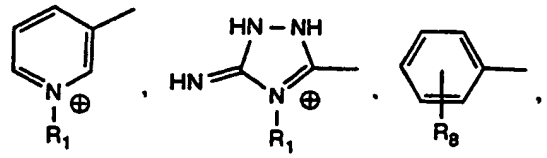
R_5 is hydrogen, C_1-C_4alkoxy, halogen, C_1-C_4alkyl or C_1-C_4alkylcarbonylamino, or

R_5 and R_2 are together with the nitrogen and carbon atoms joining them together a 5- or 6-membered ring,

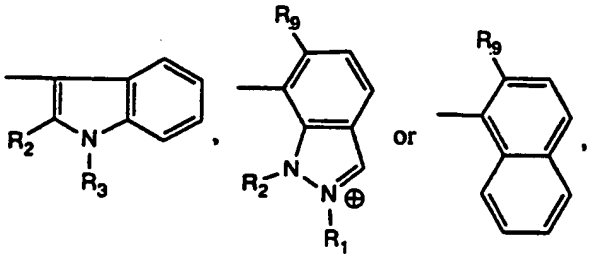
R_6 is hydrogen or unsubstituted or OH-, C_1-C_4alkoxy-, halogen-, CN-, amino-, C_1-C_4monoalkylamino-, di-C_1-C_4alkylamino- or tri-C_1-C_4alkylammonium-substituted C_1-C_4alkyl,

R_7 is hydrogen, unsubstituted or OH-, C_1-C_4alkoxy-, halogen-, CN-, amino-, C_1-C_4monoalkylamino- or di-C_1-C_4alkylamino-substituted C_1-C_4alkyl or C_1-C_4alkoxy,

D_1 is the radical of a diazo component of the formula



K is the radical of a coupling component of the formula



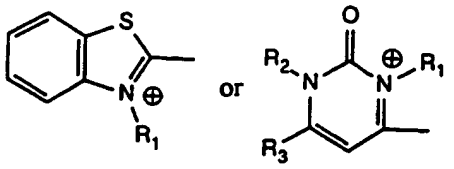
with the proviso that either D_1 or K carries a cationic charge,

R_8 is hydrogen, C_1-C_4alkyl, C_1-C_4alkoxy, halogen or amino,

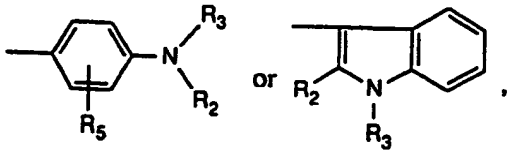
R_9 is hydroxyl or amino

A is CN or tri-C_1-C_4alkylammonium-substituted C_1-C_4alkoxycarbonyl,

B is a radical of the formula



E is a radical of the formula



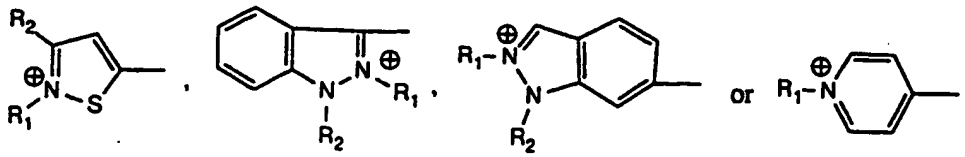
R_{10} and R_{11} are independently of each other hydrogen or unsubstituted or OH-, C_1-C_4alkoxy-, halogen-, CN-, amino-, C_1-C_4monoalkylamino- or di-C_1-C_4alkylamino-substituted C_1-C_4alkyl, or
R_{10} and R_{11} are together with the nitrogen atom joining them together a 5- or 6-membered ring, and
$An^{\ominus}$ is a colourless anion.

2. A process according to claim 1, wherein the dye used has the formula (1) or (2).

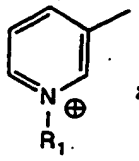
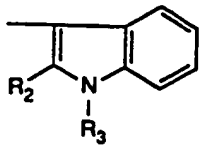
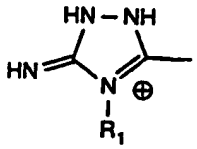
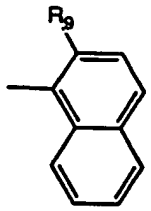
3. A process according to either of claims 1 and 2, wherein the dye used has the formula (1) where R_1 is unsubstituted C_1-C_4alkyl, especially methyl or ethyl.

4. A process according to any one of claims 1 to 3, wherein the dye used has the formula (1) where R_5 is hydrogen, methoxy, ethoxy, chlorine, methyl or ethyl.

5. A process according to any one of claims 1 to 4, wherein the dye used has the formula (1) where D is the radical of a diazo component of the formula



where R_1 is unsubstituted C_1-C_4alkyl, especially methyl or ethyl, and R_2 is hydrogen or unsubstituted C_1-C_4alkyl, especially methyl or ethyl.

6. A process according to claim 1, wherein the dye used has the formula (2) where D_1 is the radical of a diazo component of the formula  and K is the radical of a coupling component of the formula  or the formula (2) where D_1 is the radical of a diazo component of the formula  and K is the radical of a coupling component of the formula  where R_1 is unsubstituted C_1-C_4alkyl, especially methyl or ethyl, R_2 and R_3 are independently of each other hydrogen or unsubstituted C_1-C_4alkyl, especially methyl or ethyl, and R_9 is hydroxyl or amino.

7. A process according to claim 1, wherein the dye used has the formula (3) where A is CN, R_5 is hydrogen or unsubstituted C_1-C_4alkyl, especially methyl or ethyl, R_2 is unsubstituted C_1-C_4alkyl, especially methyl or ethyl, and R_6 is tri-C_1-C_2alkylammonium.

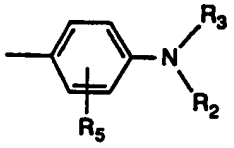
8. A process according to claim 1, wherein the dye used has the formula (3) where A is tri-C_1-C_2alkylammonium, R_2 and R_6 are independently of each other hydrogen or unsubstituted C_1-C_4alkyl, especially methyl or ethyl, and R_5 is hydrogen, methoxy, ethoxy, chlorine, methyl or ethyl.

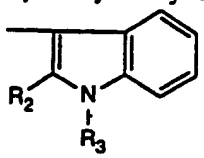
9. A process according to claim 1, wherein the dye used has the formula (4) where R_1 is unsubstituted C_1-C_4alkyl, especially methyl or ethyl, and R_2 and R_5 are independently of each other hydrogen or unsubstituted C_1-C_4alkyl, especially methyl or ethyl.

10. A process according to claim 1, wherein the dye used has the formula (5) where R_1 is unsubstituted C_1-C_4alkyl, especially methyl or ethyl.

11. A process according to either of claims 1 and 10, wherein the dye used has the formula (5) where R_2 and R_3 are independently of each other hydrogen or unsubstituted C_1-C_4alkyl, especially methyl or ethyl.

12. A process according to claim 1, wherein the dye used has the formula (6) where R_1 is unsubstituted C_1-C_4alkyl, especially methyl or ethyl, and E is a radical of the formula



or


, where R_2 and R_3 are independently of each other hydrogen or unsubstituted C_1-C_4alkyl, especially methyl or ethyl, and R_5 is hydrogen or unsubstituted C_1-C_4alkyl, especially hydrogen.

13. A process according to claim 1, wherein the dye used has the formula (7) where R_1 is unsubstituted C_1-C_4alkyl, especially methyl or ethyl.

14. A process according to either of claims 1 and 13, wherein the dye used has the formula (7) where R_2 and R_3 are independently of each other hydrogen or unsubstituted C_1-C_4alkyl, especially methyl or ethyl, and R_{10} and R_{11} are each hydrogen.

15. A process according to claim 1, wherein the dye used has the formula (8) where R_1 is unsubstituted C_1-C_4alkyl, especially methyl or ethyl.

16. A process according to either of claims 1 and 15, wherein the dye used has the formula (8) where R_2, R_3, R_{10} and R_{11} are each independently of the others hydrogen or unsubstituted C_1-C_4alkyl, especially methyl or ethyl.

17. A process according to claim 1, wherein the dye used has the formula (9) where R_1 and R_2 are each unsubstituted C_1-C_4alkyl, especially methyl or ethyl.

18. A process according to any one of claims 1 to 17, wherein the fibres are treated with a mixture of at least two cationic dyes of the formulae (1) to (9).

19. A process according to claim 18, wherein the fibres are treated with a mixture of at least three cationic dyes of the formulae (1) to (9).

20. A process according to claim 19, wherein the fibres are treated with a mixture of a yellow, a red and a blue cationic dye of the formulae (1) to (9).

21. A process according to any one of claims 1 to 20 for dyeing live human hair.

22. A process according to any one of claims 1 to 20 for dyeing hairs of domestic animals.

23. A process for dyeing hairs of live animals and humans, which comprises using one of the processes of claims 1 to 20 together with colorimetric methods of measurement to obtain predeterminable shades.

24. A cosmetic formulation for hair dyeing comprising at least one of the dyes of the formulae (1) to (9) as set forth in claim 1 and also further assistants.

25. A process for dyeing hair on live animals and humans, which comprises using a mixture of at least two ready-prepared dyes of the formulae (1) to (6), preferably a mixture of a yellow, a red and a blue dye, together with colorimetric methods of measurement to obtain predeterminable shades.

INTERNATIONAL SEARCH REPORT

Inter. ..nal Application No
PCT/EP 94/03826

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A61K7/13

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR,A,2 140 205 (L'OREAL) 12 January 1973	
A	FR,A,2 282 860 (L'OREAL) 26 March 1976	
A	DE,A,41 37 005 (CHEMIE AG BITTERFELD -WOLFEN) 13 May 1993	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 January 1995	17.02.95

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Klaver, T

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INTERNATIONAL SEARCH REPORT

Inter. ..nal Application No
PCT/EP 94/03826

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
FR-A-2140205	12-01-73	BE-A-	784359	04-12-72
		CA-A-	1021324	22-11-77
		CA-A-	1020463	08-11-77
		CH-A-	560539	15-04-75
		DE-A-	2227214	14-12-72
		GB-A-	1360562	17-07-74
		LU-A-	63287	22-01-73
		US-A-	3869454	04-03-75
		US-A-	3985499	12-10-76
		US-A-	4151162	24-04-79
		LU-A-	64565	16-07-73
FR-A-2282860	26-03-76	LU-A-	70835	19-08-76
		BE-A-	832887	01-03-76
		CA-A-	1051875	03-04-79
		CH-A-	581997	30-11-76
		DE-A-	2538363	13-05-76
		GB-A-	1491930	16-11-77
		US-A-	3985499	12-10-76
		US-A-	4151162	24-04-79
DE-A-4137005	13-05-93	NONE		